THE DETERMINATION OF TANNIN BY METALLIC OXIDES.¹

BY WILLIAM H. KRUG. Received September 6, 1895.

THE following experiments were suggested by a method proposed for the estimation of tannin by Mr. Kerr, associate reporter on tannin, during the progress of the official work for the Association of Official Agricultural Chemists. This method consisted of the percolation of the tannin-bearing liquor through a column of asbestos with which a certain amount of vellow mercuric oxide had been intimately mixed. After making a number of attempts to obtain concordant results. I found it too difficult to secure uniform conditions such as rate of percolation, extent of contact and uniformity in the asbestos laver, and therefore turned to find some other way of using the oxide. It then occurred to me to substitute it for the hide-powder in the ordinary shaker method. During the work I extended the investigation to three other oxides, viz., magnesium, zinc, and lead oxides.

At the beginning it was evident that much more time would be consumed in absorbing the tannin in this manner and a number of preliminary experiments were made to determine this time limit if possible. In all cases when, upon filtration after shaking a certain length of time, it was found that combination was incomplete, the solution was allowed to stand until this was accomplished. It was thus found, that with magnesium and mercuric oxides, it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration.

With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed. These two oxides were, therefore, rejected as requiring too much time, though the analyses made with them, are given below for comparison.

The extract used contained 42.35 per cent. soluble solids, and the diluted liquor used in the analyses, contained two grams of this extract per 100 cc. This diluted extract gave in twenty-

¹ Read at the Annual Meeting of the Association of Official Agricultural Chemists, Sept. 5, 1895. five cc. as a mean of three determinations, 0.0113 gram ash, containing 0.0006 gram magnesium oxide.

The tannin was determined by the loss insolids, *i.e.*, twentyfive cc. of the filtrate were evaporated on the steam-bath in a weighed dish, dried three hours in a water-bath, and the weight of the residue determined. The difference between this weight and the solids in twenty-five cc. of the original diluted extract, was taken as tannins. The ash determinations were made as a check on the amount of the oxide dissolved during the analysis.

Experiments with zinc oxide.

_	N	fethod.			Z11O	a luted extract	filtrate evapo-	Weight of	Per cent. tannin in extract.	Grams ash in	Granis ZnO in ash.
Shakeu	4 hour	s, stood	over	night	2.0	75	25	0.1095	26.45	0.0125	0.0008
••	4 ''	••	••	••	2.0	75	25	0.1174	(8.87	0.0147	0.0019
Shaken	4 110111	s, stood	one	week	···· 2 .0	75	25	0.1049	21.37	0.0095	
**	4 **	••	••	••	2 .0	75	25	0.1029	21.97	0.0103	0.0030
••	4 '*	••		••	2.0	75	25	0.1029	21.47	0.0100	0.002 0

The first two of these analyses gave a faint reaction for tannin, but were run through so as to compare the result with those obtained with other oxides. The low figures indicate incomplete combination. The last three gave no test for tannin when filtered, and agree fairly well. They are low, compared with lead and mercury oxides, and agree better with the results obtained with magnesium oxide. The amount of zinc oxide dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxide is the slow action. The last three analyses were tested every day for a week, before it was found that all the tannin had been absorbed. For this reason zinc oxide would be of no value in a laboratory where the rapid estimation of tannin is desired.

Experiments with lead oxide.

		Meth	od.			РЬО	luted extrac	t evapo-	Weight of	Per cent. tannin in extract.	of ash from	Grams PbO
Shaken	31 1	hours.	stood	2	days	4.0	75	25	0.0738	27.59	0.0111	o
- 6	31	••	••	2		•••4.0	75	25	0.0754	27.27	0.0092	0
••	32	• •		2	••	4.0	75	25	0.0706	28.23	0.0105	0

None of these gave a reaction for tannin with ferric chloride. The results were higher than with any other oxide used. The objection to lead oxide is the length of time required for complete combination.

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Ch.h	_	- 1 1		thod	l. ood over	a í or h t	MgO used.	extract used.	filtrate evapo- rated.	Weight of	Per cent. tannin in extract. 19.67	ash in resi-	Weight MgO in ash. 0.0055
				•		<u> </u>		75	25				
" "	:	2 🛓	. (4		• 6	•••2.0	75	25	0,1028	21.79	0.0195	0.0042
**	:	21	"	•	• ••		20	75	25	0.1230	17.75	0.0232	0.0052
" "	:	21	**	1		"	2.0	75	25	0.1246	17.43	0.0247	0.0058
Stood	24	hou	ITS W	rith o	ccasiona	alsh'l	c'g 2.0	75	50	0,2063	21.72	0.0252	0.0074
"	24	"		"	"	"	2.0	75	50	0.2061	21.74	0.0244	0.0076
••	24	"		**	• ''	• •	2.0	75	25	0.1157	19.21	0.0213	0.0044
•1	24	• •		f 1	••	14	2,0	75	25	0.1114	20.07	0.0205	0.0038
"•	48	"		" "	**	**	2,0	75	50	0.1941	22.94	0.0326	0.0064
••	48	"		۰ ¢	• •		2.0	75	50	0.1959	22 .76	0.0339	0.0070
Shak	en	31 1	nour	s, ste	ood over	night	t2.0	75	50	0.2165	20.70	0.0349	0.0102
×4		31	"•		••	"	2.0	75	50	0.2191	20.44	0.0355	0,0111
"		31	"	1		" "	2.0	75	50	0.2179	20.5 6	0.0359	0.0115

Experiments with magnesium oxide.

This table shows that a considerable amount of the oxide is dissolved, and passes into the filtrate, increasing the weight of the residue, and correspondingly lowering the tannin. That this error may be quite considerable is shown by the fact that in almost every estimation, the ash is almost double that found in the original diluted extract. Furthermore, this error does not seem to be constant, so that no correction can be made for it.

Experiments with mercuric oxide (yellow).

			Metho	od.		Grams HgO used.	extrac	filtrate t evap-	Weight of	Per cent. tannin in . extract.		veight gO in ash.
Stood	48 ho	urs w	ith occ	asiona	al sh'l	¢'g 4.0	75	25	0.0833	25.69	0.0070	0
••	48 ''	. '	•	••	"	4.0	75	25	0.0829	25.77	0.0077	0
••	48 ''	•	•	**	"	4.0	75	25	0.0829	25.77	0.0071	0
Shak	en 1}	hours	, stood	lover	night	t4.0	75	25	0.0842	25.51		••
**	2	"	• •	٠.		•••4.0	75	25	0.0867	25.01		••
••	31	"	" "	4 4	**	•••4.0	75	25	0.0863	25.09	0.0081	0
. (31	"	16	6.		4.0	75	25	0.0860	25.15	0.0080	0
	4	"	• •	"	" (•••4.0	75	25	0.0839	25.57	0.0084	0
•1	4	• 4	" "	• '	" (4.0	75	25	0.0849	25.37	0.0065	0
"	4	"	• •	۰.	"	•••4.0	75	20	0.0638	26.41	0.0065	0
	4	"	۴.	: :	"	•••4.0	75	20	0.0692	25.05	0.0103	0
" "	4	+1	"	" "	"	•••4.0	75	20	0.0682	25.29	0.0094	0
••	4	"	"	"	••	•••4.0	75	25	0.0863	25.09	0.0083	o
	4	۴.	**	• 1	**	4.0	75	25	0.0849	25.37	0.0097	0
••	4	41	**	**	"	•••4.0	75	25	0.0842	25.51	0.0084	0

The above analyses show that even though the conditions may be varied, fairly concordant results can be obtained with mercuric oxide as long as care is taken to ensure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed, since, when it is reached, the yellow oxide no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tanninextract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several too ec. sugar flasks, which are of a convenient size for this work.

THE ESTIMATION OF SULPHUR IN REFINED COPPER.³

BY G. L. HEATH. Received September 4, 1 95.

S EVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius¹ proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hampe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

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¹ Read at the Springfield Meeting.

² Zischr. anal. Chem., 13, 223.